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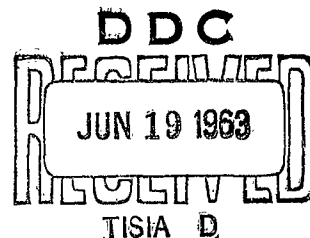
THE EQUILIBRIUM BETWEEN PEROXYDISULFURYL DIFLUORIDE
AND FLUOROSULFATE FREE RADICALS.

by

Francis B. Dudley and George H. Cady

Department of Chemistry
University of Washington
Seattle 5, Washington

1963



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Contribution from the Departments of Chemistry, University of Washington, Seattle, Washington and the University of New England, Armidale, N.S.W., Australia.

The Equilibrium Between Peroxydisulfuryl Difluoride
and Fluorosulfate Free Radicals.

By Francis B. Dudley¹ and George H. Cady.

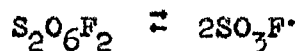
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1. Work done at the University of Washington while on sabbatical leave from the University of New England, Armidale, N.S.W., Australia.
-

Peroxydisulfuryl difluoride and fluorosulfate free radicals have been shown to exist in equilibrium below 600°K². The

2. In a prefluorinated nickel vessel that had been conditioned with $S_2O_6F_2$ to render it inert to $S_2O_6F_2$ and dissociation or decomposition products.
-

temperature dependence of pressure at constant volume was used to calculate a series of K_p values between 450°K and 600°K. This method indicated an enthalpy change of 22.1 kcal/mole whereas a spectrophotometric method based on the temperature dependence of the absorption of the fluorosulfate radical at 474 mμ, gave an enthalpy change of 23.5 kcal/mole.

The known chemistry of peroxydisulfuryl difluoride provides strong evidence for the equilibrium



Rupture of the relatively weak O-O peroxy linkage in the otherwise strongly bonded parent material, results in two fluorosulfate radicals which add readily to molecules with ethylenic double bonds (e.g. perfluoroethylene and perfluorocyclopentene³) and which will replace even chlorine from a large number of halogen containing

3. Jean'ne M. Shreeve and George H. Cady, J.A.C.S., 83, 4521 (1961).

organic and inorganic molecules³.

The oxidizing capacity and structural stability of this fluorosulfate radical is shown by the ability of peroxydisulfuryl difluoride to oxidize substances such as nitric oxide⁴, nitrogen

4. John E. Roberts and George H. Cady, J.A.C.S., 82, 353 (1960).

dioxide⁴, iodine⁵, bromine⁵, sulfur dioxide⁶ and sulfur tetrafluoride³

5. John E. Roberts and George H. Cady, J.A.C.S. 82, 352 (1960).

6. John E. Roberts and George H. Cady, J.A.C.S. 82, 354 (1960).

to fluorosulfate derivatives. The preparation of peroxydisulfuryl difluoride by anodic oxidation⁷ of a solution of an alkali metal

7. F. B. Dudley, J.C.S. (In press).

fluorosulfate in fluorosulfuric acid, or from metallic fluorosulfates⁷ by displacement reactions involving the use of elementary fluorine, are both strongly suggestive of the intermediate formation of fluorosulfate radicals.

Of similar equilibrium systems, involving dissociation of a molecular species into two free radicals, that which has been most extensively studied is the nitrogen tetroxide-nitrogen dioxide equilibrium^{8,9}, whilst a recently investigated one is that between

8. Bodenstein, Z. Physik, Chem. 100, 68, (1922).

9. F. Verhoek and F. Daniels, J.A.C.S., 53, 2250 (1931).

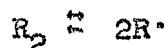
tetrafluorohydrazine and the difluoroamino radical¹⁰.

10. F. A. Johnson and C. B. Colburn, J.A.C.S., 83, 3043 (1961).

When gaseous samples of the dimeric parent material were heated to about 100°, a yellow color developed. Convincing evidence that this was due to a reversible dissociation is provided by Fig. 1 which shows the temperature dependence of the visible and ultra-violet absorption spectrum in the 320-600 millimicron region, at a constant concentration of the peroxy compound. The absorbance measurements in this wave-length range were reproducible with increasing and decreasing temperatures up to 120°. Above this temperature, reaction apparently occurred with the quartz cell, and on cooling the cell, the measured absorbance was always less than that recorded at a corresponding temperature during heating. As a result, equilibrium constants for the reversible dissociation were not obtained from spectrophotometric measurements by a procedure like that used by Johnson and Colburn¹⁰ in their investigation of the dissociation of tetrafluorohydrazine. The fine structure that is evident between 474 and 500 mμ is presumably due to electronic transitions to different vibrational energy levels in the excited electronic state.

The concentration dependence of the absorbance at constant temperature is evident from the experimental data shown in Fig. 2, but is further emphasized by Fig. 3 which shows plots of absorbance versus the square root of the concentration of the peroxydisulfuryl difluoride at constant temperature.

The linear relationship shown in Fig. 3 is to be expected for any equilibrium



if $C_{R_2} \gg C_{R^{\cdot}}$, where these symbols refer to the concentration of the undissociated and dissociated species respectively. In this study R_2 is $S_2O_6F_2$ and R^{\cdot} is considered to be SO_3F^{\cdot} . Since $A = C_{R^{\cdot}} \epsilon l$ (where A is absorbance, $C_{R^{\cdot}}$ is the concentration of the absorbing species, ϵ is the molar absorptivity index in liters/mole-cm, and l is the path length in cm), K_0 the equilibrium constant in terms of concentration is given by

$$K_0 = \frac{(C_{R^{\cdot}})^2}{C_{R_2}} = A^2 / (\epsilon^2 l^2 C_{R_2}) .$$

It follows that

$$\ln K_0 = 2 \ln A - \ln \epsilon^2 l^2 C_{R_2} .$$

If the absorptivity index is temperature independent and any change in C_{R_2} is negligible by comparison with $C_{R^{\cdot}}$, a plot of $\log A$ versus T^{-1} should be a straight line, having a slope corresponding to the change in internal energy for the reaction. The least squares "best fit" of the experimental spectrophotometric absorbance data to an equation of the form $\log A = B \times 10^3 T^{-1} + C$ gave the results shown in Table 1. for seven samples having different concentrations. An average for the internal energy change (as obtained from the slopes

Table 1

Least Squares "Best fit" Equations

$$[\log A = B \quad T^{-1} + C]$$

$10^3 \times C_{R_2}$ moles liter ⁻¹	B	C	ΔH
2.887	2.483	8.1094	23.49
7.668	2.492	8.451	23.59
12.63	2.458	8.440	23.24
17.42	2.535	8.459	23.94
22.17	2.435	8.431	23.03
27.39	2.401	8.408	22.71
49.30	2.457	8.681	23.24

of these lines) is 22.7 kcal/mole. This corresponds to an enthalpy change of 23.3 kcal/mole at 298°K.

Equilibrium constants and a confirmation of the spectrophotometric enthalpy value were obtainable from observations of the pressure variation of $S_2O_6F_2$ samples with temperature. The radical is stable up to 600°K in a nickel vessel that has been suitably conditioned (see experimental section), and above 400°K dissociation is sufficient to cause measurable deviation from the ideal gas laws. Obviously, results obtained at higher temperatures could be expected to be most reliable as errors in observed departures from ideal gas behavior would then be less significant. This is emphasized in Fig. 4, where the $\log K_p$ values farthest removed from the least squares best fit linear plot are those corresponding to the lower temperatures.

In calculating the extent of dissociation at any particular temperature, it was necessary to know the pressure expected in the event of no dissociation occurring. This was calculated from the observed initial pressure assuming ideal gas behavior and after making due correction for the volume expansion of the reaction vessel.

The experimental data for 6 runs over an initial pressure ranging from 42 to 218 mm. at 330°K were combined and a least squares "best fit" gave the equation

$$\log K_p = 7.981 - 4.785 \times 10^3 T^{-1}$$

which yields a value of 22.0 kcal mole⁻¹ for the enthalpy change.

The linear dependence of absorbance on the square root of the concentration of the parent material only requires a reversible dissociation into two parts not necessarily identical. Similarly the temperature dependence of both absorbance and pressure can be explained on the basis of non identical dissociation products. To the authors it seems almost certain that each of the two molecules formed by the dissociation of one molecule of peroxydisulfuryl difluoride is a fluorosulfate free radical. The color, the speed with which equilibrium is attained and the formation of fluorosulfates by chemical reactions of peroxydisulfuryl difluoride are all properties to be expected from dissociation into fluorosulfate radicals. No other stoichiometrically possible pair of molecules (For example $\text{SO}_3\text{F}_2 + \text{SO}_3$) which the authors have considered would give the observed properties of the system.

Experimental.

Spectrophotometric. — A Beckman Model D.U. quartz spectrophotometer and 5 cm quartz cylindrical cells were used at a wavelength of 474 mμ for all absorbance measurements. Temperatures, constant to within $\pm 0.1^\circ$, could be maintained by use of a specially constructed temperature regulated cell holder and furnace. Temperatures were measured with a thermocouple. A stopcock and 10/30 connection was sealed to the quartz cell, which was evacuated and weighed, prior to the introduction of a suitable quantity of $S_2O_6F_2$ under vacuum transfer conditions. The peroxydisulfuryl difluoride in the cell was then condensed with liquid oxygen and the inlet tube sealed. The weight of sample present was then obtained by difference. After completion of each run, the inlet tube was cut, the cell washed out and the volume of the tube and cell obtained by filling with water and weighing. This permitted a calculation of the concentration of $S_2O_6F_2$ used. Kel-F fluorocarbon grease was used on all stopcocks and ground glass connections.

Pressure variation with temperature at constant volume. — These measurements were carried out in a 1500 cc. prefluorinated nickel reaction vessel, the surface of which was further conditioned first by exposure at 250° to sulphur trioxide vapor, and later to successive batches of peroxydisulfuryl difluoride. Prolonged pumping after each treatment ensured complete removal of any volatile materials. This conditioning process was aimed at producing a surface that would be inert to peroxydisulfuryl difluoride and its dissociation product.

Because the substances involved react with mercury, pressure measurements were made with a calibrated Booth-Cromer pressure transmitter rather than directly with a mercury manometer. The

temperature of the reaction vessel was measured at several points by chromel-alumel thermocouples, and during use, was found to be the same over the surface of the vessel within a range of 0.5° . The peroxydisulfuryl difluoride used in this work was prepared by the method of Dudley and Cady¹³, its purity being checked by I.R. spectra,

13. F. B. Dudley and G. H. Cady, J.A.C.S., 79, 513 (1957).

and by determinations of molecular weights and oxidizing power. Suitable quantities were introduced into the reaction vessel by vaporizing the material from the sample tube at room temperature. The reaction vessel was cooled during this process, if pressures in excess of 120 mm were required.

After introduction of the peroxydisulfuryl difluoride, the temperature of the reaction vessel was gradually raised to a maximum of 600°K , and then allowed to cool to room temperature, pressures being recorded at regular temperature intervals. The pressure-temperature graphs were, within the limits of experimental error, identical with both increasing and decreasing temperatures. Above 600°K , decomposition commenced. The pressure-temperature curves for falling temperature were no longer the same as for rising temperature and the final product contained sulfuryl fluoride and oxygen.

After each run not exceeding 600°K samples were found to be quantitatively condensable, and to give the same I.R. spectrum as the original material.

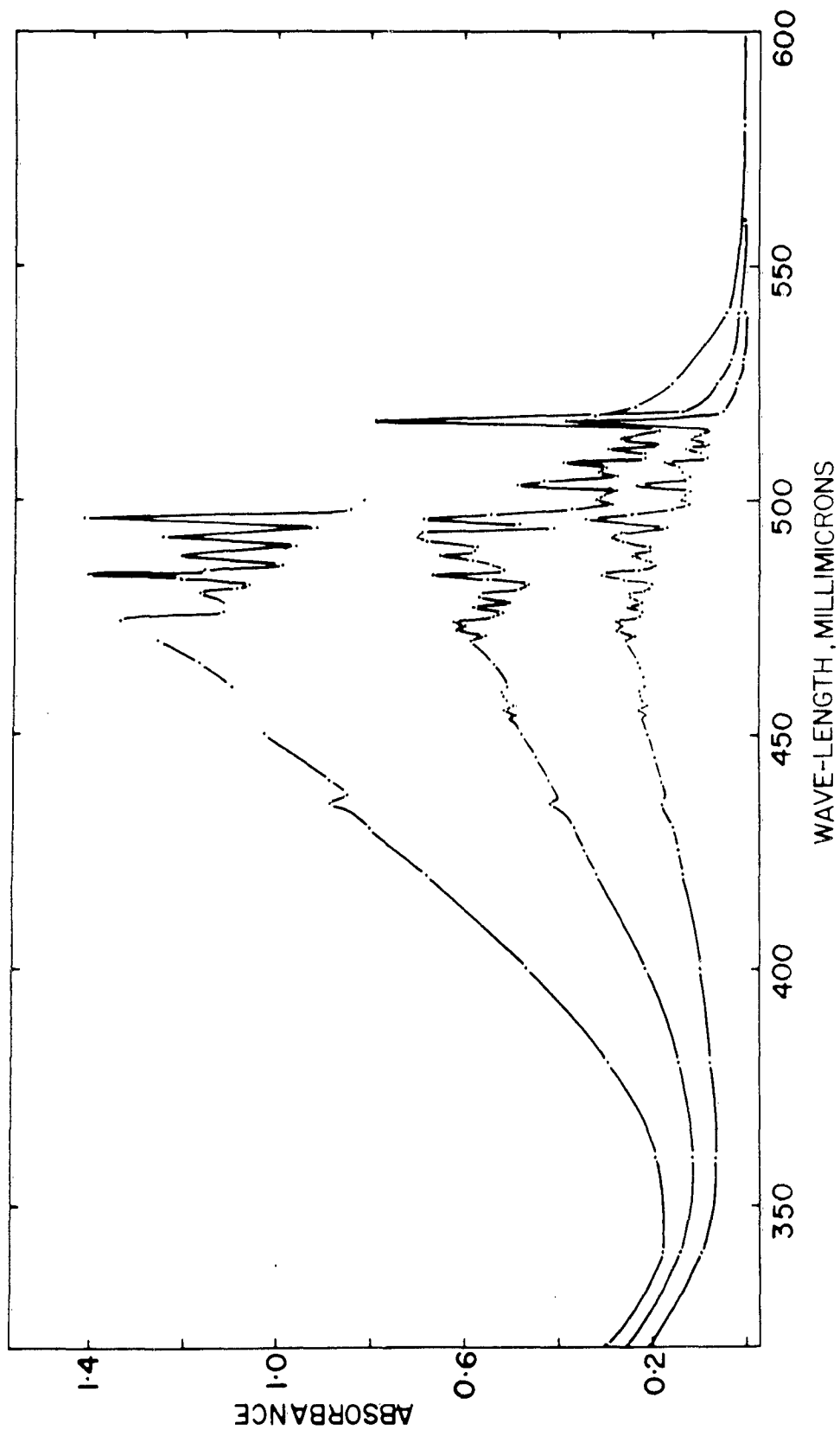


Fig. 1. The temperature dependence of the u.v. and visible absorption spectrum of peroxydisulfuryl difluoride in the wave-length region of 320 to 600 milli-microns. Temperatures at which the three spectra were taken were 106°, 88°, and 70° respectively.

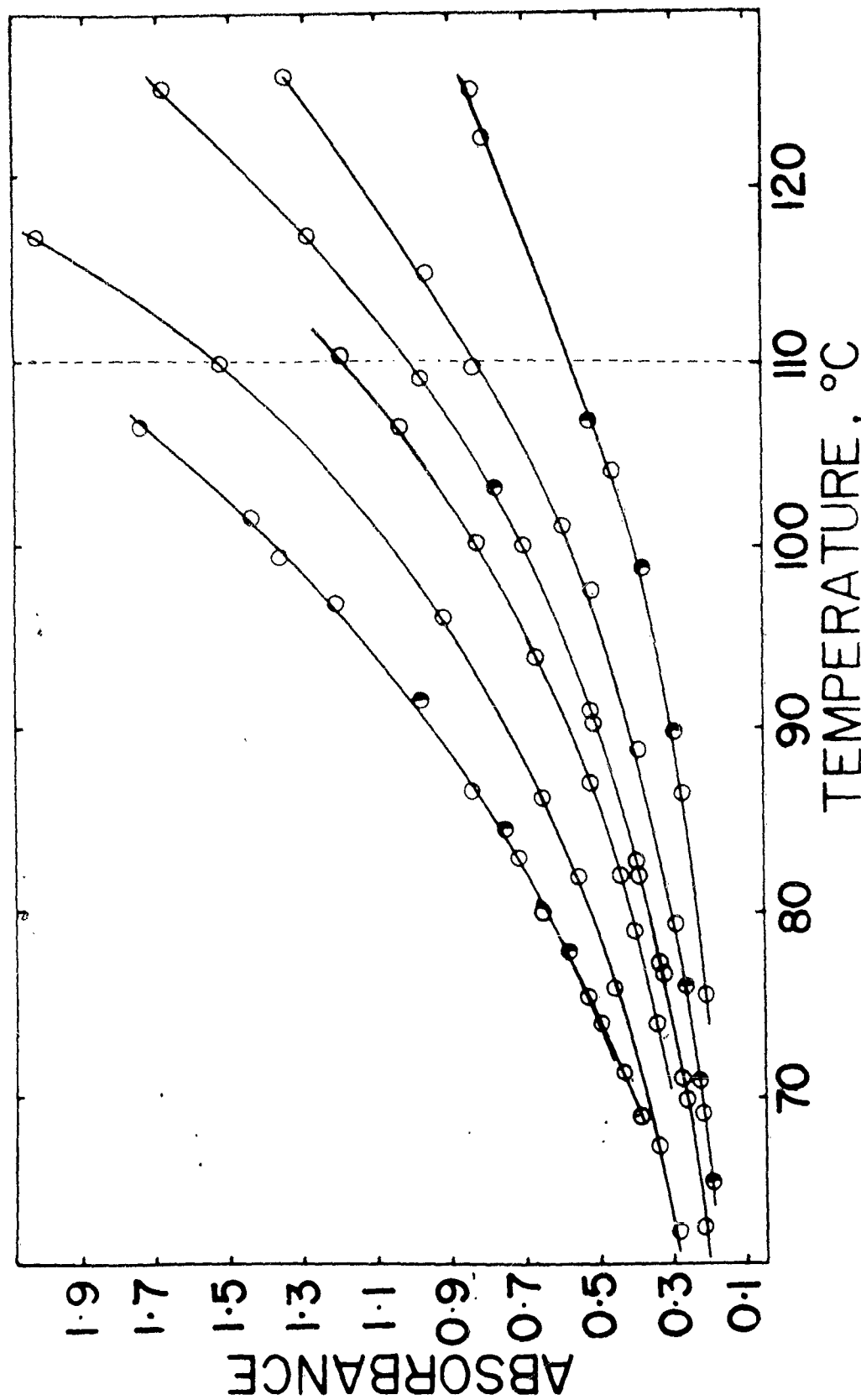


Fig. 2. Combined temperature and concentration dependence of absorbance. Any isotherm (---) indicates the concentration dependence. Absorbance curves at equal concentrations (---) show the temperature dependence. Concentrations in millimoles liter⁻¹ were in increasing order 2.887, 7.668, 12.63, 17.42, 27.39 and 49.30. Measurements taken with increasing temperature are shown O, those with decreasing temperature by ●.

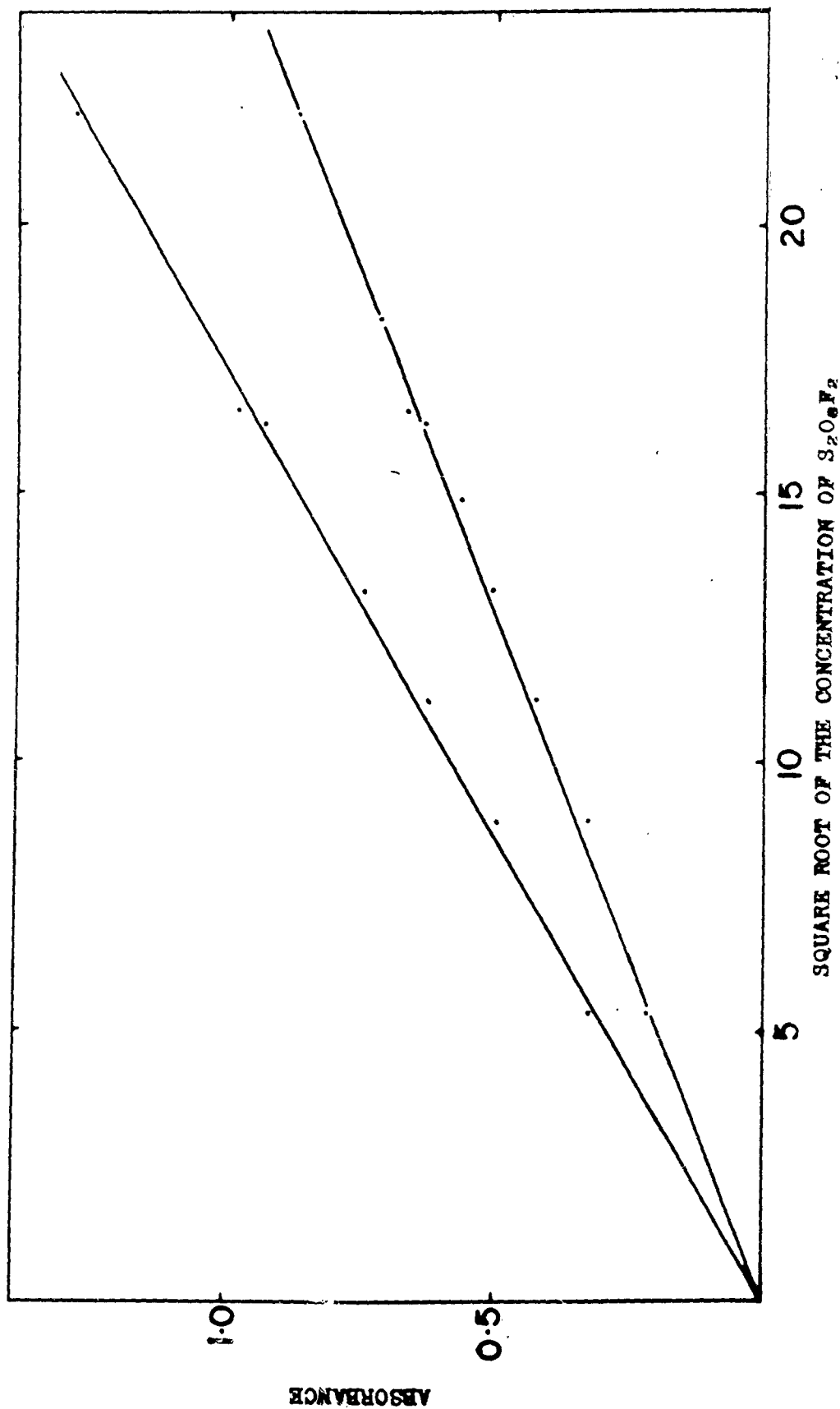


Fig. 3. Absorbance versus the square root of the concentration of peroxydisulfuryl difluoride (The relative pressures would be in the same ratio as the concentrations for fixed temperatures)

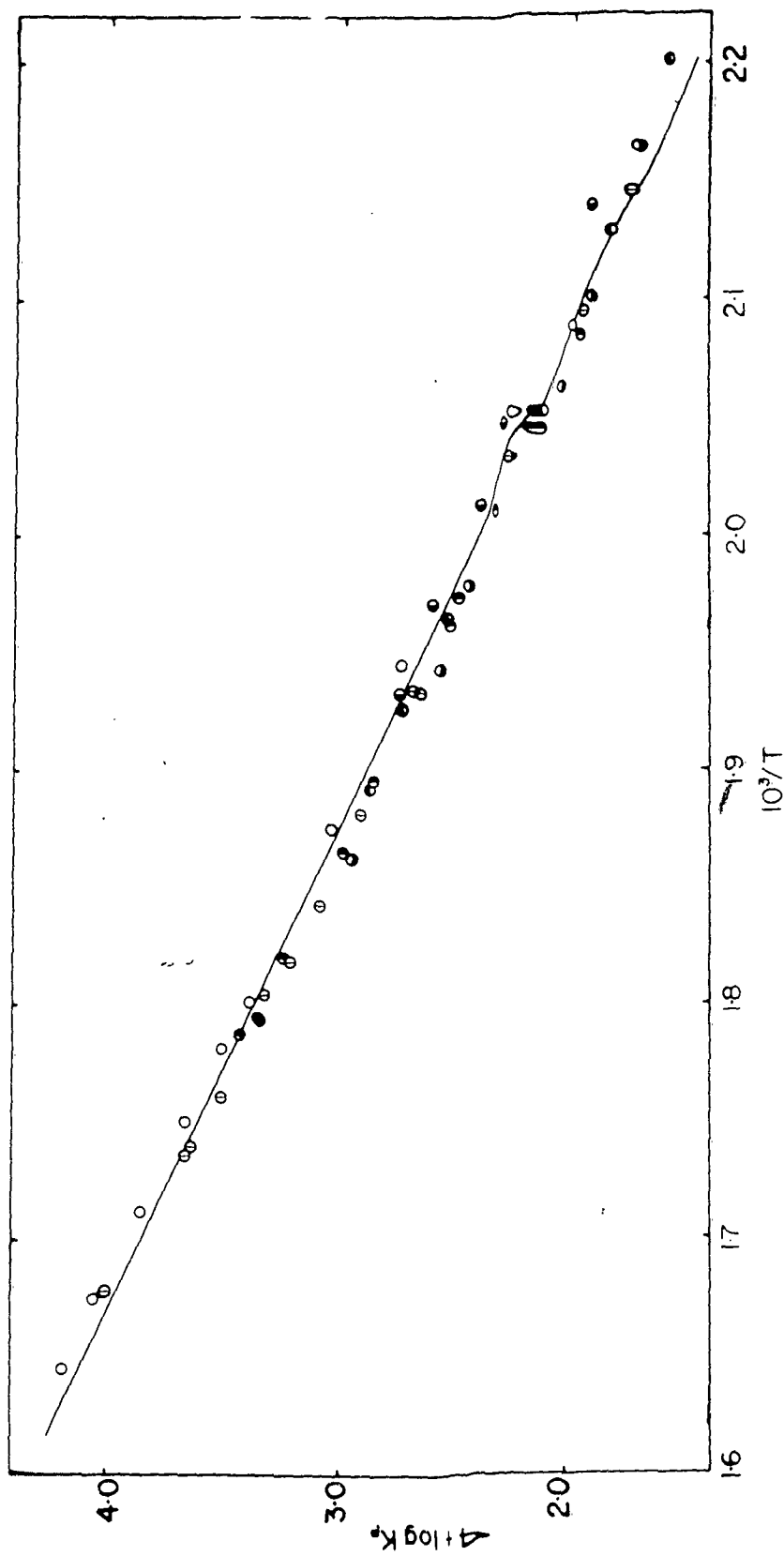


Fig. 4. $\log K_p$ versus 10^3T^{-1} plot of pressure variation with temperature data on assumption of the reversible dissociation $S_2O_8F_2 \rightleftharpoons 2SO_3F$. For the various runs, the pressures of gas in mm at 350°K were as follows: O 232; O 176.2; O 169.5; O 147.7; O 88.0; O 45.5.